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NaCl multi-layer islands grown on Au(111)-(22 × $\sqrt{3}$) probed by scanning tunneling microscopy

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Abstract

The growth of multi-layer NaCl islands on Au(111)-(22 × $\sqrt{3}$) surfaces was investigated using scanning tunneling microscopy (STM). We observed that the aspect of the NaCl islands drastically differs depending on the tunneling conditions. It is therefore possible to observe the layers forming an NaCl island or to image the gold reconstruction below the first NaCl layer. Atomically resolved STM images obtained on the first NaCl layer demonstrate that NaCl grows as an epitaxial crystalline film on Au(111)-(22 × $\sqrt{3}$). STM images also suggest that some NaCl layers can be non-crystalline.

(Some figures in this article are in colour only in the electronic version)

Intense research efforts have been focused on the preparation of oxide surfaces and insulating thin films for potential applications in the field of nanotechnology and nanoelectronics [1]. These materials are promising substrates to support nanostructures when the aim is to decouple their electronic states from those of the support and to reduce charging effects. Insulating thin films have been successfully employed to explore properties of nanostructures: for example, it has been possible to address and probe the electronic states of a single molecule [2] and of a single metal particle [3], to control the charge state of a single adatom [4], to observe the interactions between spins in individual nanostructures [5], and to flip the spin of a single adsorbed atom [6]. These oxide and insulating surfaces are also interesting for technological applications. They have been used to control the growth of fcc metal nanocrystals [7] and five-fold twinned structures [8, 9], and to enhance the catalytic activity of metal nanoparticles [10].

Silica [11, 12], vanadium oxide [13], alumina [2, 12], ceria [14], iron oxide [15, 16], magnesium oxide [17], titania [10], strontium titanate [18–20], and sodium chloride [4, 21–27] are some of the promising materials to support and electronically isolate nanostructures for technological

application. Among these materials, sodium chloride is not only very versatile, it also has the great advantage of growing as layers. NaCl islands have indeed been successfully grown on numerous crystalline metal surfaces, such as Cu(111) [4, 21, 22], Cu(110) [4, 21], Cu(311) [21], Ag(111) [23], Ag(100) [24], Ge(100) [25], Al(111) [26], and Al(100) [27].

Bulk sodium chloride is an ionic crystal with cubic symmetry consisting of positively charged sodium ions, Na⁺, and negatively charged chloride ions, Cl[−], figure 1(a). Each of these ions is surrounded by six ions of opposite charge. This crystallographic structure maximizes the contact between ions of opposite charge. The lattice parameter of the NaCl unit cell is 5.64 Å. Sodium atoms donate their single valence electron to chlorine atoms; crystalline NaCl is therefore an insulator at low temperature.

The different faces of an ionic crystal have different electronic properties and this may strongly influence the growth and shape of ionic nanocrystals or thin films. In the case of crystalline NaCl, the (100) facet is electrically neutral, whereas the (111) facet would be polar because it consists of only one type of ion, which can be either Na⁺ or Cl[−].

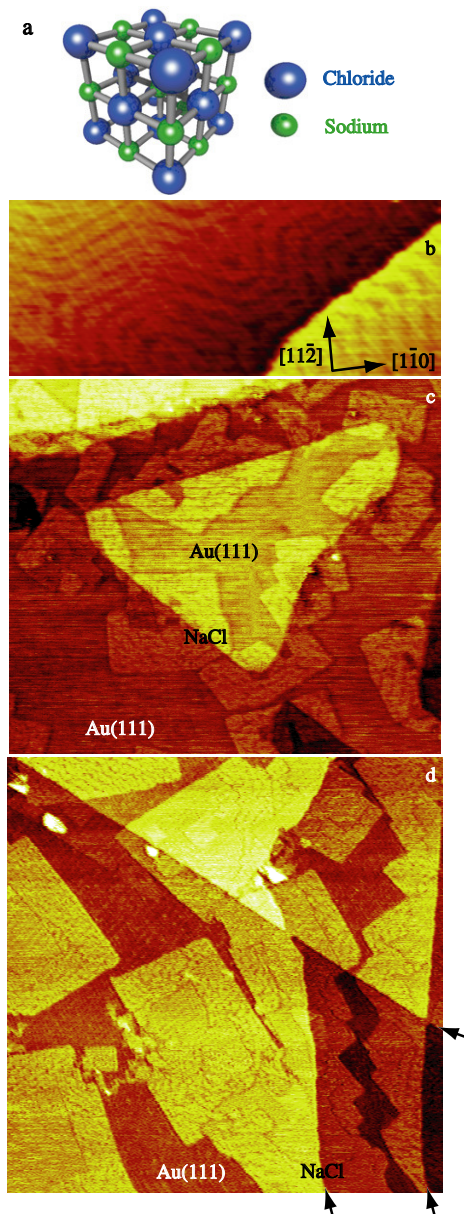


Figure 1. (a) NaCl unit cell. Blue balls are chloride atoms and small green balls are sodium atoms. (b) STM image of the Au(111)-(22 × $\sqrt{3}$) reconstruction (150 × 60 nm², $V_s = -0.70$ V, $I_t = 0.5$ nA). STM image of NaCl islands on Au(111): (c) 220 × 190 nm², $V_s = 0.80$ V, $I_t = 0.5$ nA, (d) 250 × 250 nm², $V_s = 0.38$ V, $I_t = 0.5$ nA. The black arrows point to gold step edges.

Polar surfaces usually exhibit surface reconstructions or charge reconstructions in order to minimize the charge distribution and the resulting dipole moment. In the case of NaCl, it has been experimentally shown that, depending on the growth conditions and charge distribution, (100) or (111) islands can be grown [27].

In this paper we report on the growth of NaCl islands on an Au(111)-(22 × $\sqrt{3}$) surface. We observed, using scanning tunneling microscopy (STM), that the variation of the tunneling parameters allows us to image different layers of the NaCl islands. STM images suggest that some NaCl layers are crystalline whereas the others are not.

The Au(111) substrates were prepared by sublimation of 99.99% gold (Umicore Materials AG) in a custom-built vacuum chamber having a base pressure of 10^{-7} Pa. A 250 nm thick gold film was grown on freshly cleaved mica sheets (Ted Paella, Inc.) held at 640 K. They were introduced into the ultrahigh vacuum (UHV) chamber of a scanning tunneling microscope (Omicron AFM-STM) operating at a pressure of 10^{-8} Pa, and repeatedly sputtered with argon ions (500 eV) and annealed at 500 °C typically for 45 min. The formation of a reconstructed Au(111)-(22 × $\sqrt{3}$) surface was then checked by STM; see figure 1(b). The step height of a gold terrace was measured to amount to 2.35 Å, which corresponds to the gold plane separation in the [111] direction. Ideally, the Au(111) surface reconstructs into a herringbone pattern, but often this surface forms a complicated pattern of paired corrugation lines [28, 29]. These paired corrugation lines are aligned with the $\langle 11\bar{2} \rangle$ gold direction and repeat periodically every 6.3 nm. NaCl was sublimated at 450 °C onto the gold substrate in the preparation chamber and then transferred to the STM chamber for imaging. Cut PtIr wire was used as the STM tip to obtain constant current images at room temperature with a bias voltage V_s applied to the sample. The STM images were processed and analyzed with FabViewer [30].

Figures 1(c) and (d) show STM images of NaCl islands formed after deposition of NaCl on an Au(111)-(22 × $\sqrt{3}$) surface at room temperature. These islands have almost straight step edges and the angle between the step edges is $\sim 90^\circ$. The small NaCl islands are mostly located on top of gold step edges. This suggests that gold step edges are preferential nucleation sites for NaCl islands; see figure 1(c). Further NaCl deposition leads to the growth of NaCl islands forming large domains; see figure 1(d). The STM images show that the second and third NaCl layer start to form on the first one before the latter completely covers the Au surface.

Figure 2 presents similar NaCl islands on Au(111) imaged by STM with two different tunneling conditions, namely -0.3 V @ 0.15 nA (a) and -1.0 V @ 0.7 nA (b). The gold step height of 2.3 Å was found independently of the tunneling conditions. NaCl multi-layer islands are clearly visible in figure 2(a), whereas only the first layer of same islands appears in (b). In figure 2(b) the Au(111)-(22 × $\sqrt{3}$) reconstruction is clearly visible underneath the first NaCl layer. The height profiles extracted from the images in figures 2(a) and (b) are reported in figure 2(c) and show that the first NaCl layer (figure 2(a)) has an apparent height of ~ 1.53 Å, while the thickness of the second layer in the same image amounts to ~ 0.7 Å (curve A). The height profile corresponding to figure 2(b) gives instead an apparent height of the first NaCl layer of ~ 0.9 Å, and the second layer appears ~ 1.1 Å below the gold surface (figure 2(c), curve B). The tunneling parameters are hence strongly affecting the apparent height of the NaCl layers. Even the larger value for the height of the first NaCl layer is lower than its physical height (2.82 Å). The measured height of the additional NaCl layers is even smaller, and for islands composed of three and more layers the measured height of the NaCl multi-layer islands can appear below the gold surface. These observations are a perfect illustration of NaCl non-conducting

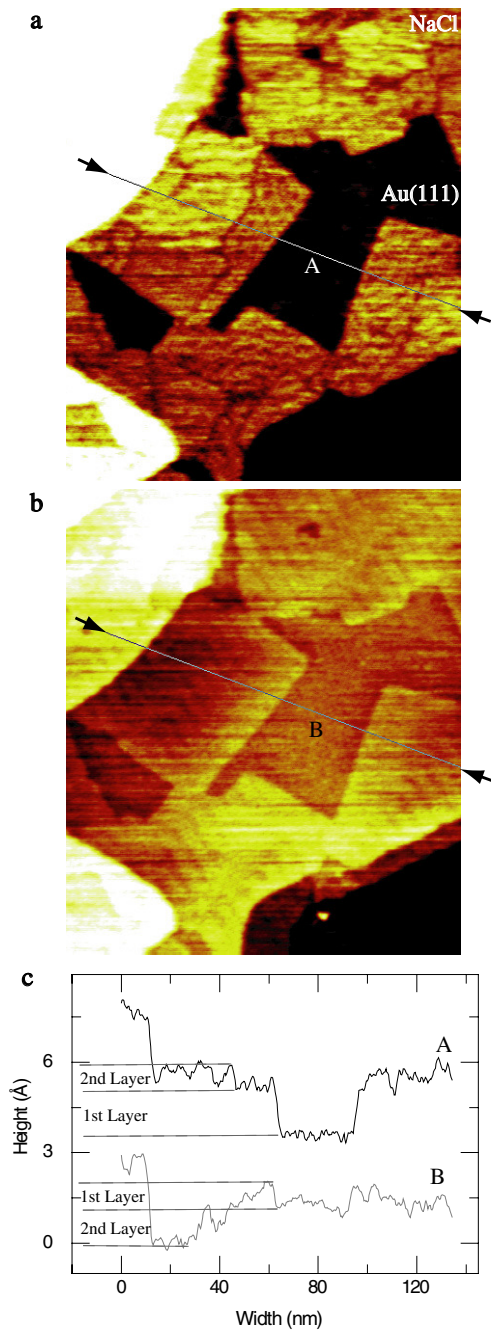


Figure 2. NaCl islands on a Au(111) surface ($140 \times 170 \text{ nm}^2$) imaged using STM with $V_s = -0.3 \text{ V}$, $I_t = 0.15 \text{ nA}$ (a) and $V_s = -1.0 \text{ V}$, $I_t = 0.7 \text{ nA}$ (b) tunneling parameters. (c) The black curve corresponds to the surface profile A extracted from (a), and the red (gray) curve corresponds to the surface profile B extracted from (b).

behavior. The NaCl layers act as a insulating thin film, which perturb the tunneling between the STM tip and the gold substrate. The formation of thicker and thicker NaCl film on the gold substrate progressively insulates the gold metal surface.

Figure 3(a) shows atomically resolved NaCl islands. From the corresponding atomic corrugation reported in figure 3(b), one sees that the distance between two nearest bright spots in the NaCl layer is $4.0 \pm 0.1 \text{ \AA}$. This corresponds to the

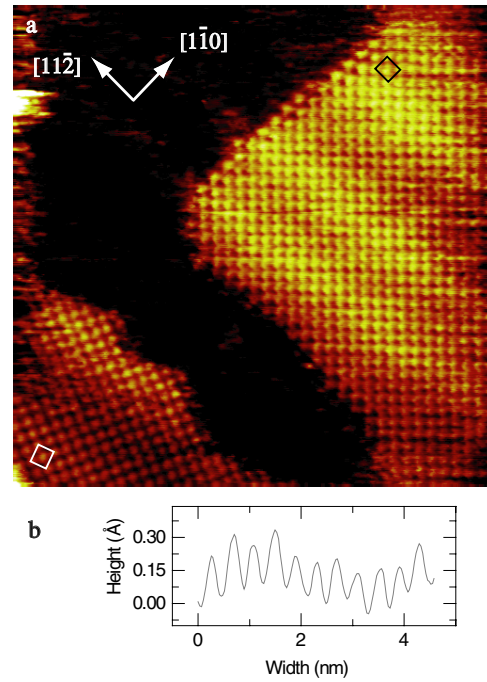


Figure 3. (a) Atomically resolved STM image of NaCl islands on Au(111)-($22 \times \sqrt{3}$) at room temperature ($16 \times 16 \text{ nm}^2$, $V_s = 0.5 \text{ V}$, $I_t = 1.0 \text{ nA}$). White and black squares representing the NaCl unit cell are superimposed on the NaCl islands. (b) Atomic corrugation of the first NaCl layer.

closest separation of one atomic species in the NaCl(001) surface. These bright spots in the NaCl island are attributed to Cl^- anions [25, 26, 31]. The atomic corrugation is $\sim 0.2 \text{ \AA}$. The atomic periodicity of NaCl is modulated by the large periodicity of the gold herringbone reconstruction, and figure 3(b) demonstrates that this reconstruction persists below the salt islands even after NaCl growth.

The STM images show that NaCl is growing as a (100) layer on the reconstructed (111) gold terraces. The square NaCl unit cell has been superimposed to each of the two NaCl layers in figure 3, as black and white squares. The two unit cells are rotated by 30° with respect to each other. The gold reconstruction visible underneath the NaCl layer shows that the NaCl unit cell is in both cases aligned with the $\langle 11\bar{2} \rangle$ and the $\langle 1\bar{1}0 \rangle$ gold directions (and equivalent directions). This indicates that NaCl grows preferentially as an epitaxial NaCl(100) film.

An NaCl monolayer will wet the Au surface if $\gamma_{\text{Au}} > \gamma_{\text{NaCl}} + \gamma_i$, where γ_{Au} is the surface energy of the Au(111) substrate, γ_{NaCl} is the monolayer surface energy, and γ_i is the interface energy between the monolayer and the substrate. $\gamma_{\text{Au}(111)} = 1.28 \text{ J m}^{-2}$ [35] and $\gamma_{\text{NaCl}(100)} = 0.16 \text{ J m}^{-2}$ [36] are obtained from *ab initio* and DFT calculations. Therefore the interface energy should be less than 1.12 J m^{-2} .

Figure 4 illustrates details of a NaCl multi-layer island as imaged by STM. The first NaCl layer appears flat while the second NaCl layer can have different aspects: the one labeled (b) in figure 4 resembles the first layer and seems flat as well; on the other hand, a complicated pattern is observed for the second NaCl layer labeled (a) in figure 4. We did

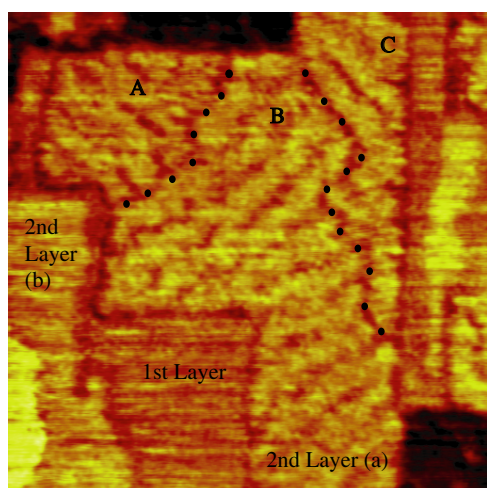


Figure 4. STM image of a NaCl multi-layer island ($68 \times 68 \text{ nm}^2$, $V_s = 0.4 \text{ V}$, $I_t = 0.5 \text{ nA}$). The first and two second NaCl layers are labeled. Three domains labeled A, B, and C coexist in the second NaCl layer labeled (a). The boundaries of these domains have been delimited with black spots for visual help.

not succeed in finding tunneling parameters permitting us to record atomically resolved images of this layer. The STM image shows that the latter is formed by juxtaposed domains of stripes labeled A, B, and C in figure 4. The patterns in these domains do not have a high degree of symmetry and are oriented differently. They therefore cannot be attributed to a Moiré pattern [24, 32, 33]. However, this suggests that the second layer is not crystalline or that its crystallization is not fully completed at room temperature, despite the fact that its edges are almost straight and nearly perpendicular. These observations illustrate that the formation of the NaCl thin film growth seems strongly dependent on the growth conditions [34].

As shown by figure 2, the NaCl layers on Au(111) act as a insulating thin film. Figure 2 shows that increasing the NaCl thickness reduces the conductivity between the STM tip and the gold substrate. NaCl thin films are promising substrates to decouple supported nanostructures from a metal support. As was done by Qiu *et al* [2] using ultrathin Al_2O_3 films, insulating thin films can be used to decrease the coupling between the molecules and their metal support with the aim of observing the vibronic states of molecules using STM. It would be interesting to investigate the decoupling and charging effects of molecules on NaCl thin films as a function of NaCl thickness. This should be achievable using low-temperature scanning tunneling spectroscopy.

In this work we have studied NaCl multi-layer islands grown on Au(111)-($22 \times \sqrt{3}$) using scanning tunneling microscopy. By changing the tunneling parameters we were able to selectively image the first NaCl layer of the islands or the other layers. Atomically resolved STM images of the first NaCl layer indicate that NaCl grows as an epitaxial (100) thin film on Au(111)-($22 \times \sqrt{3}$). STM images of some NaCl layers show non-strictly-periodic stripes, which suggest that they can be non-crystalline or not perfectly crystallized.

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